(12) UK Patent Application (19) GB (11) 2 072 401 A

(21) Application No 8106227
(22) Date of filing 27 Feb 1981
(30) Priority data
(31) 55/25912
(32) 29 Feb 1980
(33) Japan (JP)
(43) Application published 30 Sep 1981
(51) INT CL^3 G02F 1/133
(52) Domestic classification G5C A310 A342 A365 HC
(56) Documents cited None
(58) Field of search G5C
(71) Applicant
Sharp Kabushiki Kaisha
22-22 Nagaike-cho
Abeno-ku
Osaka
Japan
(72) Inventors
Toshiaki Takamatsu
Fumiaki Funada
Yutaka Ishii
Tomio Wada
(74) Agents
Venner Shipley & Co
Rugby Chambers
2 Rugby Street
London WC1N 3QU

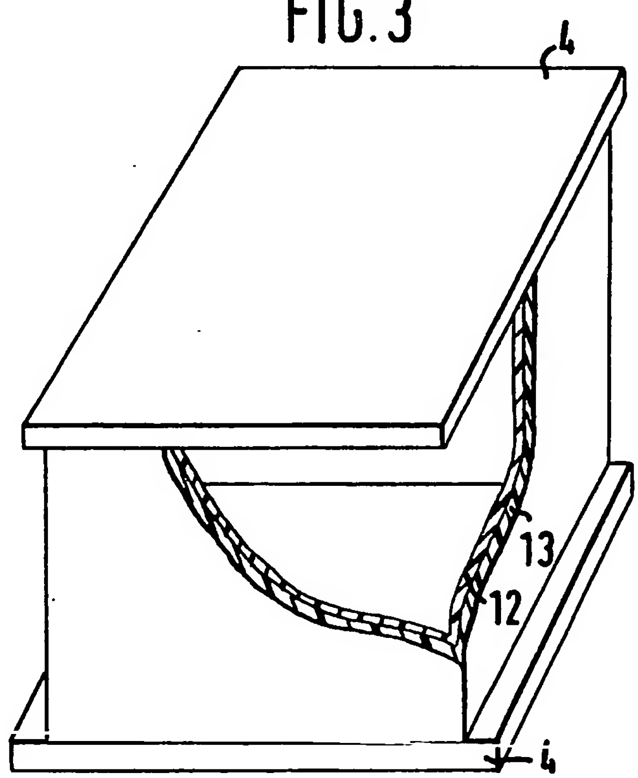
(54) Liquid crystal display device:— Sealing

(57) In a liquid crystal half-tone display device, e.g. for TV, with multiplex number N (duty cycle = 1/N), having transparent electrodes bearing insulated orienting layers on the inner faces of substrates 4 carrying polarisers, the liquid crystal material being nematic and exhibiting depolarisation, the cut-off frequency f_c (Hz) of dynamic scattering is adjusted by heavy doping to lie between 8 N.F

$$\text{and } 16 \frac{C}{C_o} \text{ N.F,}$$

where F (Hz) is the frame frequency, C is the capacitance per unit area of the insulating layers and C_o is the same for a dielectric constant of 4 and thickness 100 Angstrom. To reduce the ingress of air and moisture, the substrates are sealed with an outer ring 13 of thermoplastic polyamide surrounding an inner ring 12 of saturated polyester of higher melting point, the spacing possibly being controlled by short lengths of glass fibre in the gap.

FIG.3



The drawings originally filed were informal and the print here reproduced is taken from a later filed formal copy.
Certain of the chemical/mathematical formula(e) appearing in the printed specification were submitted in formal form after the date of filing.

GB 2 072 401 A

2072401

1/2

FIG.1

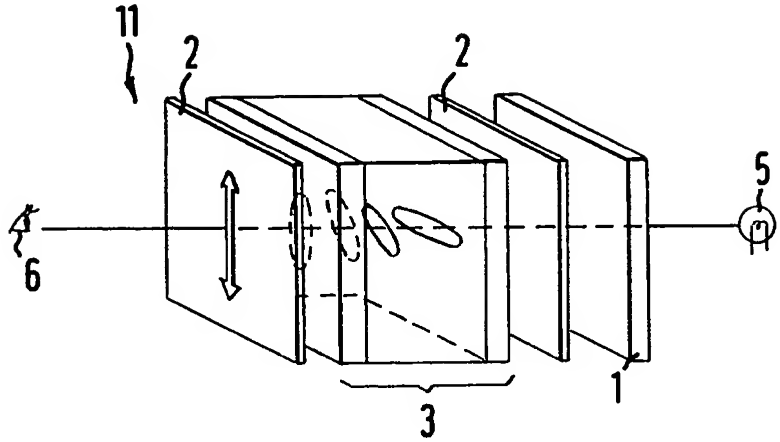


FIG.2

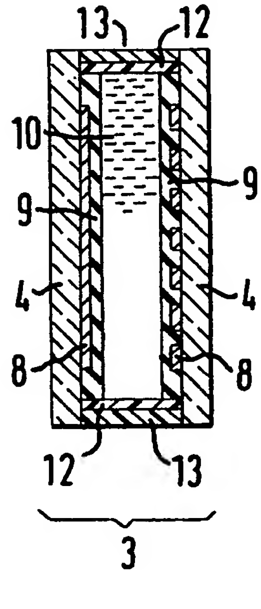
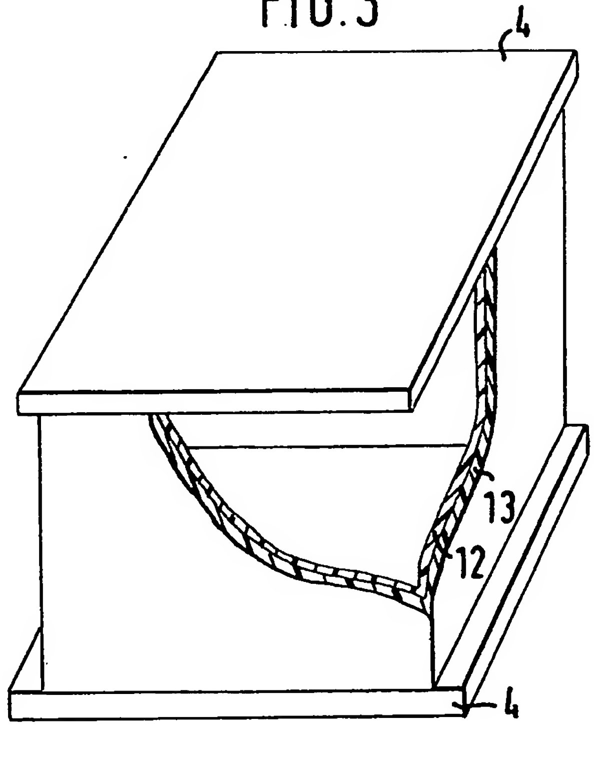


FIG.3



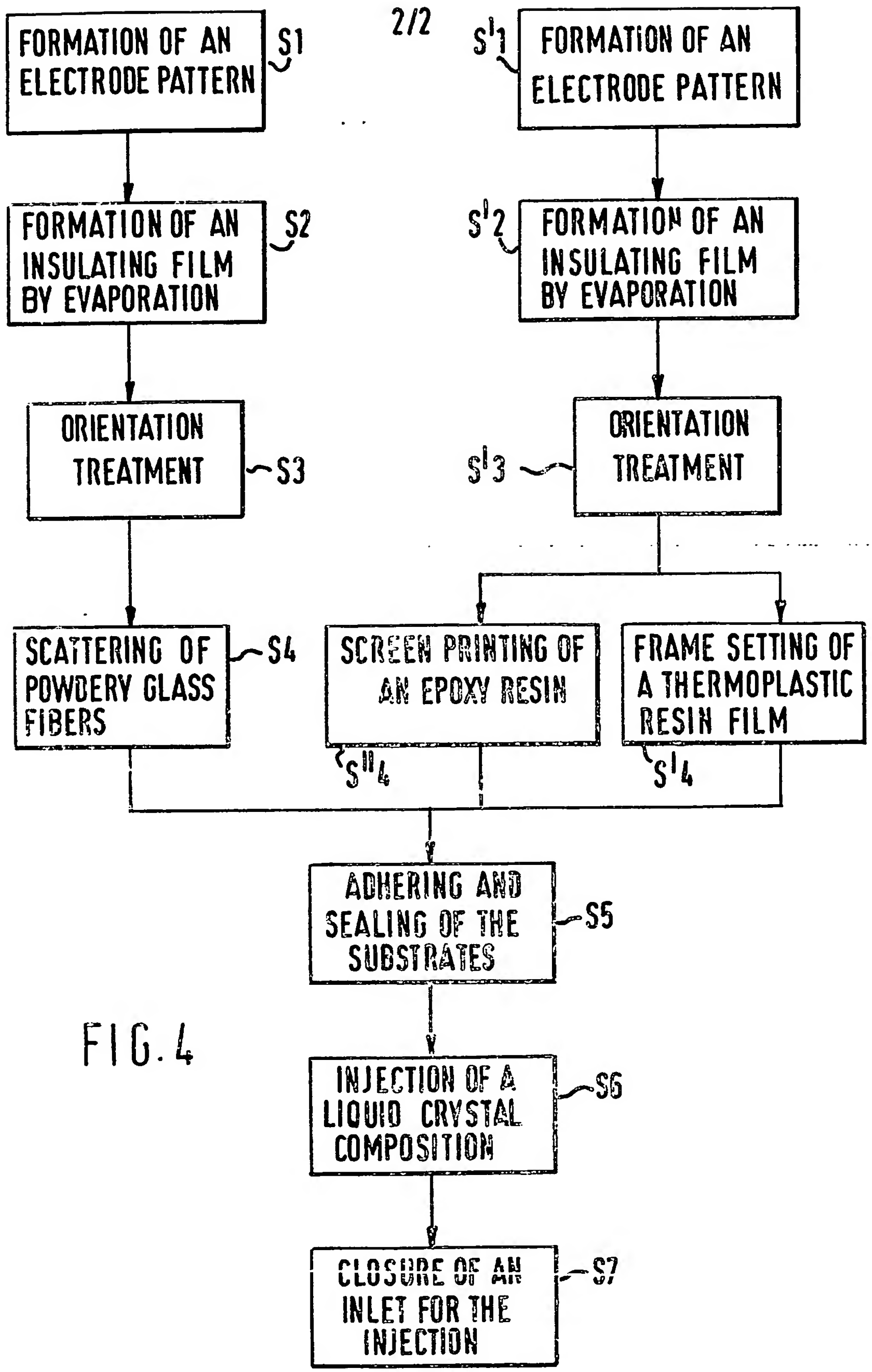

FORMATION OF AN ELECTRODE PATTERN
S1
FORMATION OF AN INSULATING FILM BY EVAPORATION
S2
ORIENTATION TREATMENT
S3
SCATTERING OF POWDERY GLASS FIBERS
S4
S'1
FORMATION OF AN ELECTRODE PATTERN
S'2
FORMATION OF AN INSULATING FILM BY EVAPORATION
S'3
ORIENTATION TREATMENT
SCREEN PRINTING OF AN EPOXY RESIN
S''4
FRAME SETTING OF A THERMOPLASTIC RESIN FILM
S'4
ADHERING AND SEALING OF THE SUBSTRATES
S5
INJECTION OF A LIQUID CRYSTAL COMPOSITION
S6
CLOSURE OF AN INLET FOR THE INJECTION
S7

FIG. 4

SPECIFICATION

Liquid crystal display devi e

The present invention is concerned with a liquid crystal display device and, more particularly, with a liquid crystal display device comprising a dynamic scattering liquid crystal cell formed by a nematic or long-pitched cholesteric liquid crystal oriented in a twisted pattern between a pair of substrates carrying transparent electrodes thereon and polarisers.

Recently, a matrix-type liquid crystal display device which is capable of displaying many kinds of information freely has drawn more attention than a conventional segment-type device. A matrix-type device has, however, its own problems. While it can display an image having improved resolution with an increase in the number of lines or electrodes, the increase in the number of the electrodes, particularly the scanning lines, leads to a reduction in the duty, i.e., the time for which a signal is applied per line and, therefore, in a cross-talk margin. If a liquid crystal is used as a display element, a satisfactory contrast is not available because of the dull transmission characteristics and slow response.

The following proposals have been made to solve the above problems:

(1) to develop a liquid crystal material having a sharp threshold and to employ a mode of liquid crystal performance showing sharp transmission-voltage characteristics;

(2) to optimise a matrix addressing system to enlarge a driving margin ($\alpha = V_{on}/V_{off}$); and

(3) to improve the electrode and panel construction to get a seemingly higher resolution.

The present invention is directed to the mode of performance referred to in (1) above. The DTN mode utilising the light depolarisation feature of the DS mode having a twist angle of 90° has recently attracted special attention. It is reported that the DTN mode is characterised by a sharp rise in the vicinity of the threshold value and a wide viewing angle and is suitable for a matrix display device having a large number of scanning electrodes (see Tatsuo Uchida, Yutaka Ishii and Masonobu Wada: "Properties of a display device using depolarisation in a twisted nematic liquid crystal layer (DTN-cell)", Proceedings of the SID, *21*(2), 55–61/1980)

However, in contradistinction to other kinds of display, such as of characters, the display of a television picture requires a halftone and the device must be capable of responding properly to a particularly high frequency component of an image signal arising from pulse width modulation. Furthermore, it is important that the proper response can be maintained for a long time.

In view of these problems, we have found it useful to incorporate a specific dopant into a liquid crystal layer and to apply a specific sealing structure to a liquid crystal cell. As a result, we have succeeded in obtaining a liquid crystal display device which is suitable for the display of an image signal, which constitutes the present invention.

According to the present invention, there is provided a novel and useful liquid crystal display device which can properly respond to any image signal with a low-to-high frequency distribution during the matrix driving of multiple lines using the DTN mode, for example in the display of a television picture, and which includes an improved sealing structure which can improve any adverse effect of an improper seal on the performance of the device.

More specifically, the present invention provides a liquid crystal display device, comprising a pair of transparent substrates defining a pair of mutually facing surfaces, a transparent electrode assembly provided on each of the mutually facing surfaces of the substrates, an insulating layer covering each electrode assembly, a DTN liquid crystal layer disposed between the mutually facing insulating layers and a polariser provided on the opposite surface of each substrate from the liquid crystal layer, wherein the liquid crystal layer contains a dopant to the extent that the cut-off frequency f_c (Hz) of the liquid crystal layer against the dynamic scattering effect satisfies the following relationship at ambient temperature:

$$16 \cdot \frac{C}{C_o} \cdot N \cdot F \gtrsim f_c \gtrsim 8 \cdot N \cdot F$$

in which N is the number of multiplex driving (hence, 1/N is the duty ratio), F is the frame frequency of an image signal, C is the capacitance per unit area of the insulating layers and C_o is the capacitance per unit area of th insulating layers when th y hav a specific di lectric constant ε of about 4 and a thickness of about 100 Å; the substat s being adh red to each other and sealed by two resin layers, in which the outer lay r is a thermoplastic p lyamide lay r and the inner layer is a saturated polyester layer having a higher melting point than the polyamide.

For a better understanding of the present invention, reference will n w be mad to th accompanying drawings, in which:

Figure 1 is a schematic view showing, by way of example, th liquid crystal display device of the DTN mode embodying th present invention;

Figure 2 is a cross-sectional view of the DS cell employed in the device shown in Fig. 1;
Figure 3 is a perspective view of the DS cell in the device of Fig. 1, which is partly broken away to show the sealing structure; and
Figure 4 is a flow chart showing the process for preparing a liquid crystal cell.

Referring first to Fig. 1, a preferred liquid crystal display devic according to the present invention is generally designated by reference numeral 11. The device 11 comprises a diffuser 1, a pair of polarisers 2 and a dynamic-scattering liquid crystal cell with a twisted-nematic alignment or DS cell 3. As shown in Fig. 2, the DS cell 3 comprises a pair of transparent substrates 4, a matrix transparent electrode assembly 8 on each panel, a pair of insulating layers 9 treated with an agent for orientation of the liquid crystal molecules, a liquid crystal layer 10 formed by a liquid crystal composition containing a dopant and a pair of sealing layers 12 and 13. Referring again to Fig. 1, 5 designates an illumination device and 6 denotes a viewer.

The construction of the liquid crystal display device according to the present invention is, however, not limited to the one as hereinabove described. The device is capable of various modifications if it essentially comprises a liquid crystal layer of the DTN type sandwiched between a pair of transparent substrates defining a pair of mutually facing surfaces each carrying thereon a transparent electrode assembly and an insulating layer treated for the orientation of liquid crystal molecules and a polariser provided on the opposite surface of each substrate from the liquid crystal layer and is suitable for use in the matrix display of, for example, a television picture.

Each transparent substrate 4 usually comprises a glass, synthetic resin or like plate. Each transparent electrode assembly 8 may usually be formed by an ITO film (consisting mainly of In_2O_3) having a thickness of 300 to 500 Å, a NESA film (consisting mainly of SnO_2) or the like. Each of the insulating layers 9 may comprise a layer of PVA or SiO_2 or a this layer of SiO_2 coated with an agent for the orientation of liquid crystal molecules or the like. It is preferable to use as thin a layer as possible in order to ensure proper response of the liquid crystal display device according to the present invention. The light diffuser 1, polarisers 2 and illumination device 5 may be selected from those known in the art.

Attention is now directed to the principal features of the present invention. Referring first to the liquid crystal layer 10, it is characterised by the quantity of dopant therein. The liquid crystal layer 10 contains a larger quantity of dopant than the liquid crystal layer in any known DS cell. This feature makes it possible to obtain an improved orientation of liquid crystal molecules, which is particularly suitable for the display of a television picture or the like.

As is well known, the driving frequency f_d for a liquid crystal display device utilising the DS effect must not be higher than the cut-off frequency f_c at which the threshold voltage for the DS effect becomes infinitely high. This relationship can be expressed as follows:

$$k_1 f_d \lesssim f_c \qquad (1)$$

in which k_1 is greater than 1.

The driving frequency f_d for the liquid crystal display device 11 can basically be expressed as follows:

$$f_d = F \cdot N \qquad (2)$$

in which F is the frame frequency of an image signal and N is the number of multiplexing of the device. Accordingly, the expression (1) can be rewritten as follows:

$$k_1 \cdot F \cdot N \lesssim f_c \qquad (3)$$

The expression (3) shows that the cut-off frequency f_c for the liquid crystal display device 11 has a certain lower limit.

When the cut-off frequency f_c is sufficiently higher than the driving frequency f_d, the DS cell 3 can be defined electrically as a serial equivalent circuit comprising a capacitance C formed by the insulating layers 9 and a resistance R formed by the liquid crystal layer 10. The voltage V actually applied to the liquid crystal layer 10 is:

$$V = \frac{E}{\sqrt{1 + \left(\frac{1}{2\pi f_d C R}\right)^2}} \qquad (4)$$

in which E stands for source voltage.

In order to obtain the voltage V r quired for application to the liquid crystal layer when the sourc voltage E is maintain d constant, th following r lationship must b maintained:

$$\frac{1}{2\pi f_c CR} \lesssim k_2 \qquad (5)$$

As is well known,

$$\frac{1}{R} = k_3 \cdot \delta \qquad (6)$$

and

$$f_c = k_4 \cdot \delta \qquad (7)$$

In view of expression (2), taken with expressions (6) and (7), expression (5) can be rewritten as follows:

$$f_c \lesssim k_5 \cdot F \cdot N \cdot C \qquad (8)$$

in which

$$k_5 = \frac{2\pi k_2 k_4}{k_3} .$$

Expression (8) also shows that the cut-off frequency f_c for the liquid crystal display device 11 has a certain upper limit.

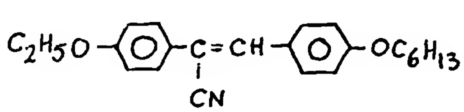
We have prepared a large number of liquid crystal display devices containing different quantities of dopant in their liquid crystal layers and have carried out a large number of experiments for the display of images. As a result, we have discovered that an image which is satisfactory in contrast and halftone can be produced if the dopant is incorporated in the quantity corresponding to the cut-off frequency f_c which satisfies expression (3) when k_1 is 8 and expression (8) when k_5 is equal to $16/C_o$, in which C_o is the capacitance per unit area of the insulating layers when they have a specific dielectric constant ε of about 4 and a thickness about 100 Å.

Therefore, in order to provide a satisfactory image display, the liquid crystal display device 11 of the present invention contains the dopant in a quantity corresponding to the cut-off frequency f_c, which satisfies the following relationship:

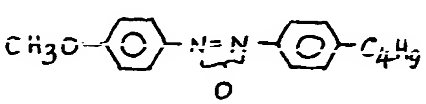
$$\frac{16}{C_o} \cdot C \cdot F \cdot N \gtrsim f_c \gtrsim 8 \cdot N \cdot F \qquad (9)$$

The quantity of the dopant thus defined is at least about 10 times larger than that which has hitherto been employed.

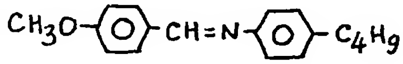
The liquid crystal layer into which the dopant is incorporated may be composed of a nematic or long-pitched cholesteric liquid crystal which is usually employed in a DS cell. It is particularly preferred to use a nematic liquid crystal of negative dielectric anisotropy, examples of such liquid crystal material including the following:

(a)  and other stilbene liquid crystals;

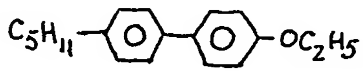
T_{CN} = 65°C. T_{NI} = 78°C.

(b)  and other azoxy liquid crystals;

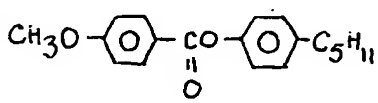
T_{CN} = 20°C. T_{NI} = 80°C.

(c)  and other Schiff liquid crystals;

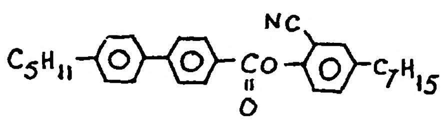
T_{CN} = 20°C. T_{NI} = 47°C.

(d)  and other biphenyl liquid crystals;

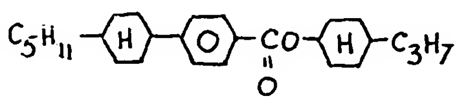
T_{CN} = 72°C. T_{NI} = 81°C.

(e)  and other ester liquid crystals;

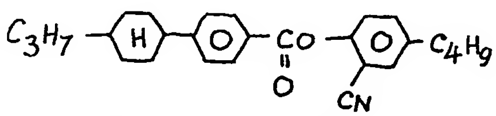
T_{CN} = 32°C. T_{NI} = 42°C.

(f)  and other biphenyl ester liquid crystals;

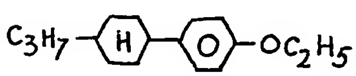
T_{CN} = 45°C. T_{NI} = 101°C.

(g)  and other phenyl-cyclohexane ester liquid crystals;

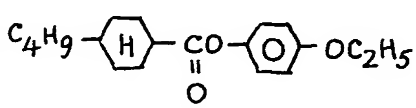
T_{CN} = 67°C. T_{NI} = 154°C.

(h)  and other phenyl-cyclohexane ester liquid crystals;

T_{CN} = 56°C. T_{NI} = 113°C.

(i)  and other phenyl-cyclohexane liquid crystals;

T_{CN} = 41°C. T_{NI} = (37°C.) monotropic

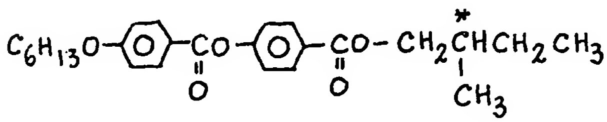
(j)  and other cyclo-hexane ester liquid crystals.

T_{CN} = 37°C. T_{NI} = 75°C.

The liquid crystal may be eith r a mixtur of liquid crystals b longing to one of the aforesaid groups or a mixture of liquid crystals selected from two or mor groups. It is also possible to use a mixture of liquid crystals other than those shown above if it has negative dielectric anisotropy. Among others, it is preferable to use a mixed liquid crystal consisting mainly of Schiff's base liquid crystal materials.

Furthermor , a minor quantity of an optically active substance, such as cholesteryl nonanoate

or

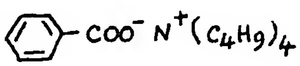


or other additives, may be incorporated in order to improve various properties of the liquid crystal layer.

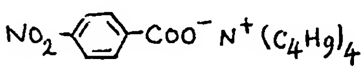
A variety of quaternary ammonium compounds known in the art may be used as the dopant in the liquid crystal display device of the present invention. Since, according to the present invention, the dopant is incorporated in a larger quantity than heretofore, it is better to used salts of organic acids, as specifically shown below by way of example, than salts of strong acids, such as $(C_4H_9)_4N^+Br^-$, since the former salts are less likely to influence the decomposition of the liquid crystal molecules.

Examples of particularly preferred quaternary ammonium compounds include the following:

(a) tetrabutylammonium benzoate



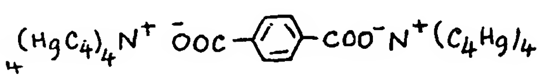
(b) tetrabutylammonium *p*-nitrobenzoate



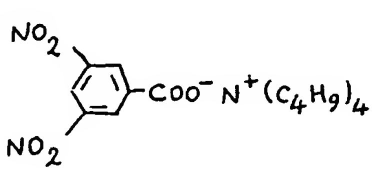
(c) tetrabutylammonium *p*-chlorobenzal-*p*'-aminobenzoate

(d) tetrabutylammonium salt of *p*-carboxybenzalamino-*p*'-chlorobenzene

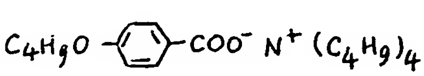
(e) tetrabutylammonium terephthalate



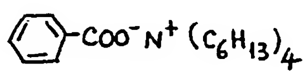
(f) tetrabutylammonium 3,5-dinitrobenzoate



(g) tetrabutylammonium *p*-but xybenzoat



(h) tetrahexylammonium benzoat



Various other compounds may be used as the dopant if they have a satisfactory solubility, electrical and electrochemical stability, freedom of any damage to the liquid crystal, durability and other factors.

According to another feature of the present invention, the liquid crystal cell has a double sealing structure composed of a sealing layer 13 of a thermo-plastic polyamide and an auxiliary sealing layer 12 of saturated polyester provided inwardly of the polyamide layer.

According to the present invention, the dopant is incorporated into the liquid crystal layer in an amount which corresponds to the cut-off frequency f_c, as hereinabove described, and which is considerably or usually at least 10 times larger than that which has hitherto been employed in a portable electronic calculator or the like.

For sealing the liquid crystal cell, use is made of a material which is capable of protecting the liquid crystal molecules in the liquid crystal layer against exposure to the atmosphere as far as possible. A liquid crystal layer composed mainly of a Schiff's base liquid crystal is particularly unstable in an electrochemical reaction or in the presence of moisture and is very likely to be affected by the atmosphere. Therefore, it has been usual practice to use a thermoplastic polyamide, an epoxy resin or the like alone for the sealing purpose. However, experiments which we have carried out indicated that those sealing materials do not satisfactorily prevent the influence of the atmosphere when a large quantity of dopant is incorporated, as mentioned above, but that the liquid crystal is likely to be affected by the atmosphere, particularly when the liquid crystal display device is used for a long period of operation, resulting in a drop in the transition point of the liquid and possibly its failure to maintain its liquid crystal state. As a result of repeated experiments, we have been able to establish a method for sealing a liquid crystal cell for a liquid crystal containing a large quantity of dopant, particularly a liquid crystal system consisting mainly of a Schiff's base liquid crystal.

Examples of the thermoplastic polyamide for the sealing layer 13 in the device of the present invention include nylon 4, nylon 6, nylon 66, nylon 69, nylon 610, nylon 612, nylon 7, nylon 8, nylon 9, nylon 11 and nylon 12, and copolymers of two or more thereof, such as nylon 6/66/12, 6/69/12, 6/610/12, 6/612/12, 6/66/11, 6/66/69/12, 6/66/610/12, 6/66/612/12, 6/66/11/12 and 6/69/11/12. It is desirable to use a polyamide or copolymer having as high a melting point as possible in order to obtain a reliable seal.

Examples of the saturated polyester for the sealing layer 12 include polyethylene terephthalate, polybutylene terephthalate and poly-1,4-cyclohexylenedimethylene terephthalate and copolymers or two or more thereof, polyethylene terephthalate being particularly preferred.

A method of adhering and sealing the substrates of the liquid crystal cell of the present invention will now be described by way of example. After a glass fibre power has been applied to each glass substrate having a desired electrode and insulating layer in order to form a spacer between the substrates, a film of a thermoplastic polyamide formed in the shape of a frame extending along the entire periphery of the substrate is placed on one of the substrates. A film of saturated polyester, formed in the shape of a frame, is then placed inwardly of the polyamide frame, i.e. on the surface facing the liquid crystal (Fig. 3). The other glass substrate is then placed on the polyamide and saturated polyester frames and the glass substrates are held under pressure by a compressing instrument and heated in order to be fused with the frames.

However, the present invention is not limited to the method described above or its adhering structure.

The film of a thermoplastic polyamide usually has a thickness of 20 to 50 μm. and preferably of about 40 μm. and the film of saturated polyester usually has a thickness of 6 to 20 μm. and preferably of about 10 μm.

It is possible to employ any heating conditions if the film of a thermoplastic polyamide can be properly fused. Thus, it is possible to obtain a double sealing structure comprising a layer of a thermoplastic polyamide and a layer of saturated polyester.

A liquid crystal containint a specific quantity of dopant is then incorporated and the injection port is closed to produce a liquid crystal cell, which cell may be used to form a liquid crystal display device according to the present invention.

The seal having a specific doubl structure in th liquid crystal display device of th pr sent invention is superior in its ability to exclude the atmospher to any conventional seal composed of a single layer of a thermoplastic polyamide, epoxy resin or the like. Th refor , even if a liquid crystal (particularly a Schiff's bas liquid crystal) containing a large quantity of dopant is used for a long period of operation, the liquid crystal is least likely to be affect d by the atmosphere (particularly by moisture pres nt ther in) and maintains a satisfactory liquid crystal state.

The liquid crystal layer in the device of the present inventi n contains a specific quantity of

dopant which is suitable for th display of an image. According to the present invention, it is possible to improve any adverse eff ct of an improper seal on the performance of the display device and to obtain an image which is satisfactory in contrast and halfton in the display of an image signal using a DTN mode with a low-to-high frequency distribution. The device of the present invention is particularly useful for the display of a television picture by commercial television broadcasting. While the frame frequency F_{TV} for commercial television broadcasting is 30 Hz, the liquid crystal display device usually employs a frame frequency which is twice as high as F_{TV}, or 60 Hz, in order to eliminate any flicker.

The present invention will now be described in further detail, by way of example.

The following Table 1 shows liquid crystal materials and an orientation agent, by way of example. The liquid crystal composition fully satisfies the cut-off frequency (exceeding 30 kHz) when a matrix display device having 120 scanning lines, an electrode structure including row electrodes centrally divided into an upper and a lower group and a frame frequency of 60 Hz is driven by the optimised amplitude-selecting method, with a driving voltage having a frequency distribution mainly in the range of 60 Hz to 7.2 kHz.

TABLE 1

Liquid crystal composition:

Liquid crystal materials:	*p*-methoxybenzylidene-*p'*-(*n*-butyl)-aniline	45 wt.%
	p-ethoxybenzylidene-*p'*-(*n*-butyl)-aniline	45 wt.%
(Additives):	1-cyano-1-(*p*-ethoxy-phenyl)-2-(*p*-hexyloxy-phenyl)-ethylene	9.82 wt.%
	cholesteryl nonanoate	0.18 wt.%
Dopant:	tetrabutylammonium 3,5-dinitrobenzoate	0.75 wt.% of liquid crystal materials
Orientation agent:	γ-glycidoxypropyltrimethoxysilane (Toray Silicone Co. Ltd.) was applied to an insulating layer of SiO_2 having a thickness of about 100 Å.	

Tests were conducted by using the liquid crystal composition and the sealing material hitherto employed in the art. Fig. 4 shows a flow chart for the process for preparing a liquid crystal cell. An insulating film of SiO_2 or the like is formed by evaporation on each glass substrate having a desired electrode pattern formed thereon and the insulating films are treated for orientation purpose (steps S_1 to S_3, or S_1' to S_3'). Spacers, such as powdered glass fibres, are applied to the whole surface of the substrates to define a uniformly wide gap between the panels (step S_4). After the substrates are sealed together, the liquid crystal composition is injected into the space defined between the substrates (steps S_5 to S_5).

Various known materials capable of screen printing were used for sealing, as is shown in the following Table 2, i.e., a combination of an epoxy resin (Somal Manufacturing Co. Ltd., R-2401) and a curing agent (Somal Manufacturing Co. Ltd., HC-11), a combination thereof with a silane coupling agent as an auxiliary bonding agent (Toray Silicon Co. Ltd., SH6040), a one-component epoxy resin (Amicon Far East Ltd., Uniset A316–8), and thermoplastic polyamides of the nylon 12 series (Daicel Chemical Industries Ltd., Diamide 2000, 3000 and 7000).

The liquid crystal cells prepared as described above were left to stand at ambient temperature in a dessicator containing water for the purpose of acceleration t st for evaluating the reliability of the sealing material against humidity. The deterioration of the liquid crystal was examined for the evaluation of the sealing material. The liquid crystal cells mploying the ab ve-mention d known sealing materials were easily affected by the atmosphere, showed a dr p in transition point and failed to maintain their liquid crystal stat . Th results of the tests are shown in the following Table 2, in which various symbols indicate the following r sults:

○ — No deterioration of liquid crystal material (virtually no chang in transition point);
△ — Partial deterioration (slight chang in transition point);

× — Virtually total deterioration (substantial change in transition point).

TABLE 2

sealing material	Testing time (hours) 100	150	200	250	300
Epoxy resins: R-2401 & HC-11 (10:3) Seal thickness: 7μm (sealing conditions: 80°C., 1 hr & 120°C., 1 hr)	×	—	—	—	—
R-2401 & HC-11 (10:3) + SH6040 (coupling agent (sealing conditions: same as above)	×	—	—	—	—
Uniset A316-8 Seal thickness: 7 μm (sealed at 150°C. for 30 min.)	×	—	—	—	—
Thermoplastic films: Diamide film 2000 (m.p. 95 to 105°C.; thickness 40 μm)	△	×	—	—	—
Diamide film 3000 (m.p. 95 to 120°C.; thickness 40 μm)	△	×	—	—	—
Diamide film 7000 (m.p. 175°C.; thickness 40 μm)	○	△	×	—	—

The diamide films were sealed at 180°C. for 30 minutes.

Similar tests were conducted for the liquid crystal cells prepared by employing the sealing material according to the present invention, i.e., a combination of thermoplastic polyamide and saturated polyester films. Sealing was carried out at about 180°C. for 30 minutes. A film of polyethylene terephthalate, having a molecular weight of 15,000 to 20,000, a melting point of 260°C. ± 1°C. and a film thickness of about 10 μm (Mitsubishi Plastic Industries Ltd., Diafoil), was used to form a saturated polyester layer. The results of the tests are shown in Table 3.

TABLE 3

sealing material	Testing time (hours) 100	150	200	250	300
Diamide film 2000 (40 μm thick) + saturated polyester film	○	△	△	×	—
Diamide film 3000 (40 μm thick) + saturated polyester film	○	○	○	△	△
Diamide film 7000 (40 μm thick) + saturated polyester film	○	○	○	○	○

It can be seen fr m Tabl 3 that the sealing structur composed of a combination of thermoplastic polyamide and saturat d polyester film provides a better protection against moisture and can protect the liquid crystal from any possibl effect of the atmosphere for a longer time than any conventional seal formed by a thermoplastic polyamid or poxy resin alone. It is particularly noteworthy that, among various thermoplastic polyamides, the use of a film having a high melting point, such as Diamide 7000 (m.p. 175°C.), lined with a saturated polyester film, can provide a very reliable liquid crystal cell. A liquid crystal display device including such a liquid crystal cell has been found to be capable of displaying a television picture which is satisfactory in contrast and halftone.

CLAIMS

1. A liquid crystal display device, comprising a pair of transparent substrates defining a pair of mutually facing surfaces, a transparent electrode assembly provided on each of the mutually facing surfaces, an insulating layer covering each electrode assembly, a DTN liquid crystal layer disposed between the mutually facing insulating layers and a polariser provided on the opposite surface of each of the substrates from the liquid crystal layer, wherein the liquid crysstal layer contains a dopant to the extent that the cut-off frequency f_c (Hz) of the liquid crystal layer against the dynamic scattering effect satisfies the following relationship at ambient temperature:

$$16 \cdot \frac{C}{C_o} \cdot N \cdot F \gtrsim f_c \gtrsim 8 \cdot N \cdot F$$

in which N is the number of multiplex driving (hence, 1/N being the duty ratio), F is the frame frequency of an image signal, C is the capacitance per unit area of the insulating layers and C_o is the capacitance per unit area of the insulating layers when they have a specific dielectric constant ε of about 4 and a thickness of about 100 Å; and wherein said substrates are adhered to each other and sealed by two resin layers, the outer layer being a thermoplastic polyamide layer and the inner layer being a saturated polyester layer having a higher melting point than the polyamide.

2. A liquid crystal display device according to claim 1, wherein the frame frequency F is 60 Hz so that the device may be used for the display of a television picture by commercial television broadcasting with a frame frequency F_{TV} of 30 Hz.

3. A liquid crystal display device according to claim 1 or 2, wherein the thermoplastic polyamide is nylon 4, nylon 6, nylon 66, nylon 69, nylon 610, nylon 612, nylon 7, nylon 8, nylon 9, nylon 11, or nylon 12 or a copolymer of two or more thereof.

4. A liquid crystal display device according to any of the preceding claims, wherein the saturated polyester comprises polyethylene terephthalate, polybutylene terephthalate or poly-1,4-cyclohexylenedimethylene terephthalate or a copolymer of two or more thereof.

5. A liquid crystal display device according to any of the preceding claims, wherein the liquid crystal layer comprises a Schiff's base liquid crystal composition.

6. A liquid crystal display device according to claim 1, substantially as hereinbefore described and exemplified.

7. A television apparatus, whenever comprising a liquid crystal display device according to any of claims 1 to 6.

Printed for Her Majesty's Stationery Office by Burgess & Son (Abingdon) Ltd.—1981.
Published at The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.